A Rapid and Accurate Method of Determining Phenols

by Edmund O. Rhodes

1912

Submitted to the School of Engineering of the University of Kansas in partial fulfillment of the requirements for the Degree of Bachelor of Science

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PREFACE.

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The investigations, which were made in order to prepare this article, were suggested to me by Dr. L. V. Redman and were carried out under his supervision. I therefore take this opportunity to acknowledge my indebtedness to him for his aid and suggestions during the time the work was being prepared.

It is the purpose of this article to present a method for the rapid and accurate determination of phenol, and to compare the results of my experiments with those which have been obtained by preceeding investigators.

Edmund O. Rhodes

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A RAPID AND ACCURATE METHOD OF DETERMINING PHENOLS

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HISTORICAL

Since the year 1871 when Landolt[1] first published a paper on the Determination of Phenol, there have been numerous attempts to find a rapid, accurate and easy method of determining phenol and each experimenter has worked under varying conditions and methods to suit his purpose. As a result of these investigations, many methods have been submitted, for which claims of more or less accuracy and rapidity have been asserted. The time required for a determination, using a bromide-bromate solution, is too long and tedious and the later methods, such as the hypobromite method of Lloyd's[2] are tacitly challenged from the fact that one of the earliest methods[3] is the standard method recommended by Pharmacopoeias at the present time.

1) Berichte 4, 770, 1871.
2) J.A.C.S. Vol 27. p. 16. 1905.
3) Zeit. fur An. Chem. 15, 233, 1876.

In 1871 Landolt suggested the use of Bromine water for the precipitation of tribromphenol. He dried this precipitate and weighed it, and determined the phenol quantitatively. The reaction upon which Landolt based his suggestion is $C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr$. This reaction is probably the best suited for purposes of quantitative determination. By his method Landolt secured results varying by 0.5 per cent or more. The chief objection to his method is the use of the disagreeable Bromine water with its attendant loss of free Bromine.

Chabrie[1] in 1898 tried to perfect Landolt's method by extracting the tribromphenol with ether and drying in a special apparatus.

Schaedler[2] in 1872 attempted to treat the phenol with sulphuric acid and determine the amount of phenyl sulphonic acid formed, by precipitating the excess of sulphuric acid by means of barium.

1) Centrbl. 1; 1309 (1898)(From Rev. Chim. Anal. Appl. 6, 138, (1898).
2) Centrbl. p.506(1872)(From Pharm.Centrbl. 13, 225).
3) Zeit fur Anal Chem. 15, 233 (1876)

In 1876 Koppeschaar[1] succeeded in shortening Landolt's method by measuring the quantity of bromine water which he added to the phenol solution and determining the excess of bromine by adding potassium iodide and titrating back with sodium thiosulphate. He substituted also for the objectionable bromine water a solution composed of potassium bromide and potassium bromate, which is now known as Koppeschaar's solution. The chief objection to this method, as recommended by Koppeschaar and U. S. P. is the fact that it works too slowly, requiring as it does one-half hour of intermittent shaking after the bromide bromate solution is added to the acidified phenol.

Chandelon[2] undertook to shorten this method and in 1882 suggested as a substitute for the bromide bromate solution a hypobromite solution, which contained sufficient KOH to hold the tribromphenol in solution. Chandelon used as an end point the disappearance of the yellow color of the solution or the failure to discolor potas-

1) Zeit fur Anal Chem. 15, 233 (1876)
2) Bul. Soc. Chim. 38, 69, (1882).

sium-iodide-starch paper. That his method was not entirely satisfactory may be seen from the fact that his results did not check better than 2 per cent. In 1878, Degener[1] used a solution of bromine water and the same indicators as Chandelon.

Very similar to Degener's method was that of Waller,[2] for it differed from the former only in the addition of a saturated solution of alum to make the precipitated tribromphenol more dense. Waller published no test analysis.

Seubert[3] obtained results which varied in percentage error from 1.5 to 3 per cent. His method was primarily, that of Koppeschaar with the exception that he used potassium-iodide-starch paper as an indicator.

Beckurts[4] in 1886 followed exactly the method of Koppeschaar. At this time he recognized the presence of tribromphenolbromide in the precipitate of tribromphenol but did not attempt to

1) J. Prakt. Chem. N.F. 17, 390 (1878).
2) Ibid. 43, 152, (1881).
3) Ber. d. Chem.Ges. 14, 1581,(1881) (from Arch. Pharm., 15, 321).
4) J. Soc. Chem. Ind. 5, 546 (1886) (from Arch. Pharm., 24, 561, (1886)

remove it because he assumed that it was quantitatively reconverted into tribromphenol by potassium iodide in acid solution. At this time Beckurts also mixed phenol with petroleum spirit, shook with a strong solution of caustic soda in a graduated flask and noted the change in volume. This method was applicable only to the approximate determination of crude phenol.

Bader[1] (1892) titrated against decinormal sodium hydroxide using symmetrical trinitro benzene as an indicator. In this case the end point was never sharp, and also, the process could not be used on solutions containing less than 2 per cent of phenol.

Messenger and Vortman[2] (1890) used an alkaline solution of iodine but this required accurate manipulation and regulation of the temperature and time in order to obtain accurate results.

Carre[3] (1891) treated phenol with nitric acid and then determined the resulting picric

1) Ztschr. Anal. Chem. 31, 58, (1892).
2) Pharm. Ztg. 29, 759. (1890).
3) Compt. Rend. 13, 139 (1891).

acid colorimetrically. This was only suited to the determination of phenol in very small quantities.

Riegler,[1] in 1899 developed a gravimetric method of weighing the precipitate with p-diazo-nitraniline. Toscher[2] (1901) oxidized in boiling alkaline solution with permanganate, and Schryver,[3] (1899), determined the "hydroxyl value" of phenol by means of the sodamide reaction. In order to use the latter method the phenol had to be perfectly dry.

Many methods for the determination of phenol in tar-oil, wine, soap, etc. have been suggested. Among these are the process of Toth[4] (1886); Kleinert[5] (1884); Fedeli[6] (1895); Giacosa[7] (1878); Endemann[8] (1899); Newberg[9] (1899); Kossler and Penny[10] (1889) and (1893) Ditz and Cedivoda[11]

1) Centrbl.(1899),II p.322(from Pharm Z #1602(1901)
2) Meyer's Jahrbuch d.Chemie p. 253 (1901) (from Moleschott's Untersuchung 15, 583)
3) J.Soc.Chem.Ind. 18, 553, (1899).
4) Ztschr. Anal Chem. 25, 160, (1886)
5) Ibid, 23, 1, (1884)
6) Ber. d. Chem. Ges. 28, 1060R (1895)
7) Ztschr. phys. Chem., 6, 43, (1878)
8)
9) Ibid, 27, 123 (1899).
10) Ibid, 17, 117 (1889)
11) Ztschr.angew.Chem pp. 873 and 897 (1899)

(1899); Stockmeier and Thurnauer[1] (1893) and others.

Lloyd in 1905[2] determined phenol in strongly acid solution by the use of a hypobromite solution made by dissolving liquid bromine in quarter normal KOH. According to the author, this method had the advantage of rapidity and accuracy. However, this method has the disadvantage that the hypobromite solution[3] may change its strength rather rapidly because of the loss of free bromine, and therefore requires frequent standardizing.

Lloyd's claim for accuracy was disputed by Olivier[4] (1909) who published results which do not agree with Lloyd's. He did not find as high a percentage of error when a large excess of hypobromite was added to the phenol as did Lloyd. He doubts the accuracy of Lloyd's numbers and methods and shows also that the length of time required

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1) Mohtr:Titrimethode 7th ed. p. 386 (1896) from Chem Ztg. pp. 119 & 151, (1893).
2) J. Am. Chem. Soc. Vol. 27, 16, (1905).
3) See page 27 of this thesis.
4) Rec. de Trav Chim. Vol 28, 362, 1909; and Ibid Vol. 29, 293, 1910.

for the Koppeschaar method with the bromide-bromate solution may be reduced from one-half hour to nine minutes. His numbers show that if the phenol solution is alkaline after the hypobromite is added, the amount of bromine disappearing in twenty-four hours will exceed that required to form tribrom-phenol by 125 per cent.

In 1908 Mascarelli[1] determined phenol gravimetrically by precipitating as tribrom-phenol-bromide from a solution containing NaBr, NaBrO and $NaBrO_3$ and acidifying with dilute HCl.

Wilkie[2] in 1911 determined phenol in the presence of sodium carbonate by means of N/10 iodine. The reaction period required for accurate results is 5-10 minutes. This method has a great advantage qualitatively, the tri-iodophenol showing in a few minutes as a precipitate when phenol is present to the extent of less than one part per million. We have tried this qualitative test and the results

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(A more complete bibliography is given at the beginning of this thesis)

1) Gaz. chim, italiana, 39, p. 180 (1909)
2) J. S. C. I. Vol XXX p. 399, 1911.

obtained agree with the author's statements. This method has the advantage of direct titration and the reaction period is reduced from one-half hour for bromine to 5-10 minutes for iodine in cold sodium carbonate solution.

APPARATUS

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Before starting upon the investigation of this subject it was necessary to arrange the laboratory in the most convenient manner possible and obtain such apparatus as would facilitate the carrying on of the experiments. As the work was to be entirely volumetric, it was necessary to have several standard solutions. These were made up in five litre bottles (brown glass or paper covered) which were fitted with siphons with glass stop cocks. The bottles were then placed on a shelf above the desk at a sufficient height to allow the filling of a burette, below the siphon.

The solutions used were N/10 thiosulphate, N/10 iodine, N/10 hypobromite, N/10 bromide-bromate and N/10 phenol (1.56 gms. per litre.), concentrated HCl sp. g. 1.2, 20% potassium iodide solution and a starch solution as indicator.

The burettes used throughout the work were standard D. R. burettes which were found to need no corrections.

A tumbling machine was devised by us for thoroughly shaking the solution. The machine consists of a long, narrow and shallow wooden box 120 cm. x 9 cm. x 9 cm. inside measurements lined on the inside with felt covered pads. This trough was made wide enough and long enough to hold twelve one-half litre bottles in a single row. The trough is fitted at one end with a grooved pulley about two feet in diameter. At the center of this pulley and also at the center of the box on the end opposite the pulley are steel spindles which fit into the wooden bearings on the supporting frame. The frame is so constructed that this box may be removed and a larger or smaller box substituted.

The motive power for the machine is furnished by a small water motor supported on an iron standard directly above the large driving pulley and connected with the latter by a small leather belt. The spped of the machine may be regulated by the tap, to which the inlet pipe of the water motor is connected. It is possible to rotate the shaker as fast as four revolutions a second, but generally, one revolution per second

was sufficient.

The bottles used in the machine were ordinary 500 cc. bottles fitted with ground stoppers and were selected from the general stock.

When it was decided to make a determination, each of the solutions was run into the bottle in the order given in the tables reading from left to right. The stopper was then placed in the bottle and while being pressed inward was given a short sharp twist. This twist brings the two ground surfaces together and makes it impossible for any of the solution to leak out or for the stopper to come out for a rate of shaking up to four revolutions per second.

The bottle is next inserted between the padded sides of the box. The pressure of the pads holds the bottle firmly in place so that revolving does not throw it out.

By this construction, the bottles are made to rotate about a central axis so that uniform shaking is insured. Moreover, no clamps are needed to hold the stoppers in the bottles during the time of shaking and the bottles are held in the

machine by the pressure of the felt pads, no straps or clamps of any kind being needed. This in particular is an advantage because by eliminating all clamps and straps, much time and labor is saved, and this was an important factor when time determinations of small duration were being made.

In our investigations we made at least two hundred determinations for which the machine was used and in no case did we experience any trouble or lose a determination on account of the apparatus. A photograph of the shaking machine appears in Fig. I.

It appeared from a study of the literature that phenol could best be determined volumetrically with a solution of hypobromite or bromide-and bromate. The present bromide-bromate method requires too long a reaction period (one-half hour) for each determination,[1] and there is no satisfactory comparison between these two methods, and the results obtained by Lloyd's hypobromite method were adversely criticized[2]. It was decided to carry

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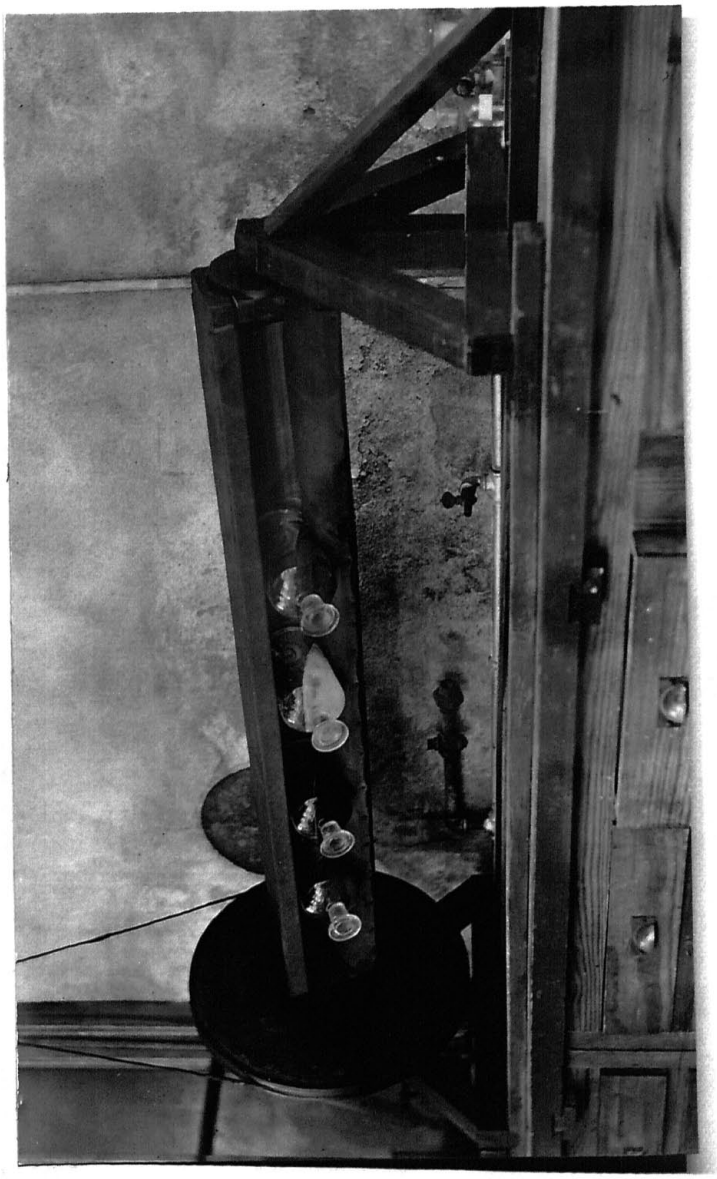
1) See A. S. P. and Koppeschaar.
2) Olivier, loc. cit.



out the determinations with these two solutions, and if possible, to come to some conclusion concerning the relative merits of the two.

With this in view there was prepared a N/10 hypobromite solution, a N/10 thiosulphate solution, a starch solution and a 20% potassium iodide solution according to the directions given by Lloyd[1] in his paper on "The determination of Phenol".

The N/10 thiosulphate solution was made up by dissolving 125 grams of sodium thiosulphate ($Na_2S_2O_3 + 5H_2O$) in five litres of water. This solution was then standardized, after it had been made up for one week, against arsenious acid and found to have the normality 0.09816.N. The starch solution was made by dissolving five grams of starch in 1 litre of water and allowing the solution to settle, and the KI solution by dissolving 20 grams of KI in 100 grams of water. The hypobromite solution was prepared by making up a quarter normal solution of KOH (70 gms. KOH in 5 litres) To this solution was then added 40 grams (12.6 cc) of liquid bromine and, the whole shaken occasionally and care-

1) J. Am. Chem. Soc. Vol. 27, Jan. 1905.

fully until the bromine was entirely dissolved by the solution. Care must be taken in shaking the bottle in which the bromine is dissolving or the bromine gas formed blows out the stopper and part of the solution may be lost.

The phenol solution required particular care because the phenol had first to be thoroughly purified. This was done by distilling three times Merck's c.p. phenol and collecting only that portion which distilled over at 182°C. 7.84 grams of this purified phenol were then weighed out and added to five litres of water (making a N 10 solution, reckoning one-sixth of a formula weight of phenol as a chemical equivalent).

When the work was first started an accident occurred which proved to be of interest later. The first four or five tests gave results indicating that almost twice as much hypobromite solution was being used as could be accounted for in the formation of tribromphenol. In other words, the indications were that instead of forming tribromphenol, some other bromine compounds were being formed. It was found that when insufficient acid

was added to the mixture of phenol and hypobromite to completely neutralize the KOH in the hypobromite solution, the absorbed bromine would always be greater[1] than that required by the phenol present to form tribromphenol.

An investigation was started to determine the effect of time of shaking and the relative concentrations of phenol and bromine present upon the results obtained. The following tables give the results of these tests. In compiling these tables the total volume was maintained at 85 cc. and only the concentration of phenol and the time of shaking while the solution was alkaline, were changed. The tables show the order of addition, reading from left to right, and volumes of materials used. The first column headed time refers to the time of shaking in minutes before the addition of the KI. The second column headed time refers to the time of shaking after the addition of KI.

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1) Olivier.

Table No. I

In this table determinations of phenol in alkaline solution were made with variable time of shaking, but with the total volume, and the quantities of phenol and hypobromite constant.

The total volume maintained throughout the table was arbitrarily taken as 85 cc. and the quantities of phenol and hypobromite as 10 cc. and 18 cc. respectively:

No.	H_2O	C_6H_5OH	KOBr	Time Min.	HCl	KI	Time Min.	Thio sulfate	Per cent
Ia	57	10	18	1	5	5	3	11.89	117.90
IIa	"	"	"	1	"	"	"	11.83	118.49
Ib	"	"	"	5	"	"	"	10.82	128.18
IIb	"	"	"	10	"	"	"	10.38	132.38
Ic	"	"	"	10	"	"	"	9.97	136.39
IIc	"	"	"	10	"	"	"	9.82	137.86
Id	"	"	"	20	"	"	"	8.87	146.96
IId	"	"	"	20	"	"	"	9.24	143.34
If	"	"	"	1 hr	"	"	"	8.81	147.55
IIf	"	"	"	1 hr	"	"	"	9.00	145.69
Ig	"	"	"	2	"	"	"	8.66	148.92
IIg	"	"	"	2	"	"	"	8.65	149.02
Ih	"	"	"	18	"	"	"	8.61	149.52
IIh	"	"	"	18	"	"	"	8.80	147.65
Ii									
IIi									

Normality of KOBr = 0.1318 N
" " Thiosulfate = 0.09816 N
" " Phenol = 0.1022 N
18 cc. KOBr 0.1318 N = 23.72 cc. N 10
10 cc. phenol 0.1022 N = 10.22 cc. N 10

Precipitate in every case was rather small and of granular nature and a yellowish color.

The percentages given in the last column are the percentages of the total amount of phenol present in the solution determined according to the above method. Instead of determining 100% of the phenol present, which would be correct, the values run from 117.9% to 147.65% or the table shows results from 17.9 to 47.65% too high; the error increasing with the time of shaking.

Table No. II.

In the following table the total volume was againg made 85 cc. and the volume of Hypobromite solution, 18 cc., but only half the volume of phenol used in Table I, viz: 5 cc.

No.	H_2O	C_6H_5OH	KOBr	Time Min.	HCl	KI	Time Min.	Thio sul-fate	Per cent
Ia	62	5	18	1	5	5	5	16.31	150.88
IIa	"	"	"	1	"	"	"	16.27	151.66
Ic	"	"	"	5	"	"	"	15.18	172.60
IIc	"	"	"	5	"	"	"	14.36	188.45
Id	"	"	"	10	"	"	"	14.60	183.75
IId	"	"	"	10	"	"	"	14.60	183.75
Ie	"	"	"	20	"	"	"	14.19	191.78
IIe	"	"	"	20	"	"	"	14.20	191.58
Ig	"	"	"	1 hr	"	"	"	13.90	197.26
IIg	"	"	"	1 hr	"	"	"	13.91	197.06
Ih	"	"	"	2	"	"	"	13.90	197.26
IIh	"	"	"	2	"	"	"	13.65	202.15
Ii									
IIi									

Normality of KOBr = 0.1318
" " Thiosulphate = 0.09816
" " Phenol = 0.1022
18cc. KOBr 0.1318 N = 23.72 cc. N 10
5 cc. Phenol 0.1022 N = 5.11 cc. N 10

No precipitates appeared after adding acid.

The results obtained by the tests made in this table show errors of percentage of phenol, ranging from 50.88% to 102.15%. Here, as in Table I, the percentage errors increase with the time of shaking. Both tables seem to approach end points after about one hour's shaking which would indicate that there is a definite end point for the particular concentration of phenol used.

Table No. III.

For the following determinations the total volume was again taken as 85 cc. and the volume of hypobromite as 18 cc., but the volume of phenol was again divided, this time making it 2.5 cc.

No.	H_2O	C_6H_5OH	KOBr	Time Min.	HCl	KI	Time Min.	Thio-sul-fate.	Per cent
Ia	64.5	2.5	18	1	5	5	3	19.81	167.84
IIa	"	"	"	1	"	"	"	19.78	169.01
Ic	"	"	"	5	"	"	"	19.04	197.25
IIc	"	"	"	5	"	"	"	19.06	196.86
Id	"	"	"	10	"	"	"	18.96	200.39
IId	"	"	"	10	"	"	"	18.94	201.17
Ie	"	"	"	20	"	"	"	18.90	202.74
IIe	"	"	"	20	"	"	"	18.89	203.13
Ig	"	"	"	1 hr	"	"	"	18.79	205.49
IIg	"	"	"	1 hr	"	"	"	18.76	208.22
I h	"	"	"	2	"	"	"		
IIh	"	"	"	2	"	"	"		
Ii	"	"	"	18	"	"	"	18.08	234.51
IIi	"	"	"	18	"	"	"	18.07	234.90

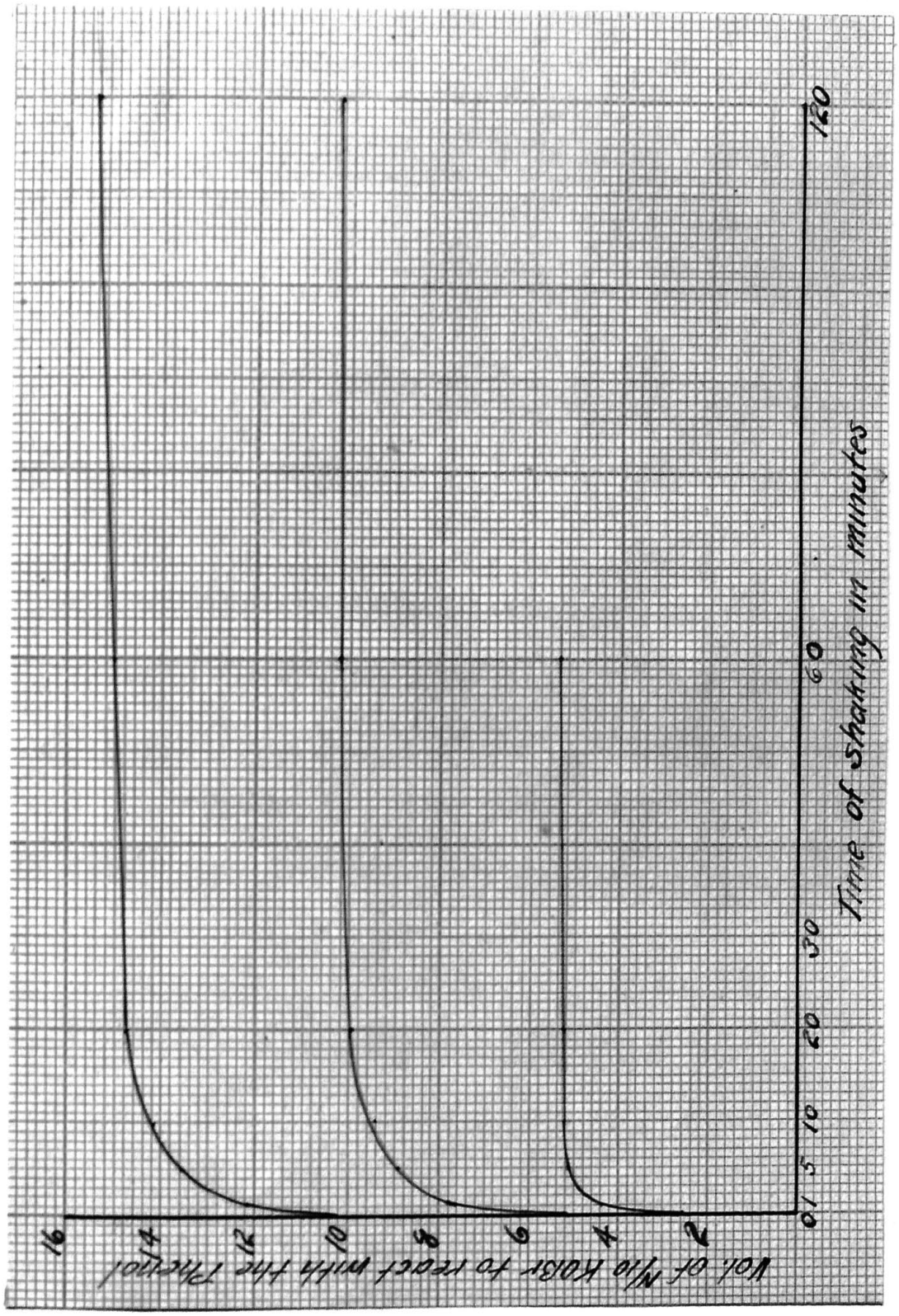
Normality of KOBr = 0.1318
" " Thiosulphate = 0.09816
" " Phenol = 0.1022
18 cc. KOBr 0.1318 N = 23.72 cc. N 10
2.5 cc. Phenol 0.1022 N = 2.55 cc. N 10

No precipitates appeared after adding acid.

By this table errors ranging from 67.84 to 134.90% are shown. As in the other cases the error increases with the time of shaking. The three tables show that with a decrease in concentration of phenol or increase in concentration ~~of~~ of the hypobromite with respect to the phenol the error in percentage is increased.

On the following page are three curves plotted from the data given in the above tables. For these curves the volume of N/10 KBrO needed to react with the phenol, and the time of shaking (in minutes) are used as coordinates. The curves show at the end of an hour the curves are becoming rapidly asymtotic.

Plate No. 2.



Curves made from data in Tables No. I, II and III "Phenol in alkaline solution"

From these tables, and from the accompanying curves, it is shown that there is a relative increase in the amount of free bromine used up as the concentration of phenol decreases and the length of time of shaking increases. It appears as if the phenol ring breaks up in alkaline bromine solution at room temperature and that it may be possible to drive the reaction completely to carbon tetrabromide[1] or a higher homologue. Several determinations were made after Table III, in which results as high as 392% of the bromine required for the determination of the phenol present as tribromphenol were obtained, which adds further evidence to the above conclusions. If 383% of the bromine used up in forming tribromphenol were absorbed, this would be enough bromine to form $2(C_2Br_6) + C_2Cr_6O$ from each reacting weight of phenol.

However, this was a decided digression from the original plan of procedure so this work was discontinued.

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1) Olivier; Rec. de Trav. Chim. 29, 294, (1910)
Collie, J. A. C. S. I, 264 (1894)
Wallach, Ann. der Chem. 275, 147 (1893)
Ibid. Ann. der Chem. 159, 322.

Returning, therefore, to the determinations ofphenol in acid solution, the hypobromite method suggested by Lloyd was the first to be tested out.

THE PERMANENCY OF A HYPOBROMITE SOLUTION.

Allen[1] states that a hypobromite solution made alkaline by dissolving 62.2 gms. of bromine in a solution containing 45 gms. of pure NaOH (this is 50% more caustic than is necessary to react with the bromine according to the equation $Br_2 + 2NaOH = NaBr + NaBrO + H_2O$) and made up to 0.16075 N. loses not more than 0.8% of its bromine by boiling it for one hour. Lloyd[2] assumes from Allen's paper that the available bromine in a solution of hypobromite is fairly constant. This is true if the bottle is kept full of solution and corked with a ground stopper. But if the ordinary 5-litre bottle be fitted up with a paraffine bark cork, siphon and inlet for air, the hypobromite solution changes its strength. A fresh solution made up in this laboratory, by dissolving 8 grams of bromine per liter

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1) J. S. C. I. Vol 3. 65. 1884.
2) J. A. C. S. Vol 27. 10. 1905.

in ~~an~~ N/4 KOH changed its strength in thirty-two days from 0.0865 N to 0.0781 N., a decrease 0.3% of strength per day. A second fresh solution of strength 0.1654 N. changed in 12 days to 0.1584 N., that is a change of 0.33% per day. A third solutionwhich was kept in a ground stoppered brown glass bottle in a dark compartment, changed from 0.1346 N. to 0.1340 N. in fifty-seven days. It is evident that this solution which was quite yellow and smelled of free bromine retained its permanency as regards available bromine when kept well corked in a brown glass bottle. This accounts for the conflicting statements made regarding the permanency of hypobromite solution. Owing to the possibility of bromine evaporating from a hypobromite solution, strongly alkaline, it is necessary to test the strength of hypobromite after each determination if these are more than a few hours apart, especially if the solution has an inlet for air to allow the siphon to operate, or if the bottle is badly corked.

THE HYPOBROMITE METHOD

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In each of the following tables, the order given from left to right is the same order in which the solutions were added for the determinations The tables show in each case the total volume, the volumes of phenol, hypobromite, HCl, KI and thiosulphate used, and also the time of shaking and the per cent of the phenol present which it was possible to determine by means of this method.

Table I was prepared in order to determine the effect of time of shaking upon the results obtained, when the total dilution, volume of phenol and volume of hypobromite solution are kept constant and the solution is acid.

The method was as follows: Into a half-litre bottle was poured 61 cc. of water. To this wass added 5 cc. of HCl sp. Gr. 1.2 and immediately following it, 15 cc. of N/10 phenol and 19 cc. of N/10 hypobromite solution. The stopper was then inserted into the bottle and the latter placed in

the shaker where it remained revolving for the desired length of time. After shaking, it was removed, five cc. of KI (20%) solution added to the mixture, and then the bottle was returned to the shaker where it revolved for at least three minutes. The following table shows the results obtained from one minute to one hour's shaking (the reaction period) before the KI solution was added.

Table IV.

Hypobromite.

No.	H_2O	HCl	C_6H_5OH	KOBr	Time Min.	KI	Time Min.	$Na_2S_2O_3$	Per cent
1a	61	5	15	19	1	5	3	3.99	100.3
1b	"	"	"	"	1	"	"	3.98	100.4
2a	"	"	"	"	5	"	"	3.97	99.7
2b	"	"	"	20	5	"	"	4.98	99.9
3a	"	"	"	19	10	"	"	3.88	100.5
3b	"	"	"	"	10	"	"	3.97	99.9
4a	"	"	"	"	15	"	"	3.89	100.4
4b	"	"	"	"	15	"	"	3.90	100.3
5a	"	"	"	"	20	"	"	3.91	100.3
5b	"	"	"	17	20	"	"	1.90	100.2
6a	"	"	"	19	30	"	"	3.88	100.5
7a	"	"	"	"	60	"	"	3.86	100.6
7b	"	"	"	"	60	"	"	3.91	100.2
8a	"	"	"	"					
8b	"	"	"	"					

Strength of Solutions KOBr = 0.1016 N
Phenol = 0.1022 N
KI = 20% solution
Thiosulphate = 0.1003
HCl = 1.2 S.G.

The results obtained above indicate that the time of shaking has very little effect upon the values obtained. It will be noticed that the values for one minute's shaking are as correct as those for one hour. There is no result in the table which varies from the correct value by more than 0.6 of one per cent and the average varies by 0.2%. This is the degree of accuracy claimed by Lloyd for the hypobromite method.

In Table No. V are given the results obtained when the concentration of the phenol with respect to the total volume was varied but the relative concentration of phenol and hypobromite were kept constant. In each case the time of shaking was 1 minute and the total dilution, 100 cc.

Table V.

No.	H_2O	HCl	C_6H_5OH	KOBr	Time Min.	KI	Time Min.	$Na_2S_2O_3$	Per cent
1a	61	5	15	19	1	5	3	3.97	100.14
1b	"	"	15	19	1	"	"	3.97	99.94
2a	83.5	"	5	6.5	1	"	"	1.50	99.79
2b	83.5	"	5	5.5	1	"	"	1.50	99.79
3a	90.4	"	3	3.9	1	"	"	0.92	99.14
3b	90.4	"	2	2.6	1	"	"	0.60	99.71
4a	92.7	"	1	1.3	1	"	"	0.32	98.90
4b	92.7	"	1	1.3	1	"	"	0.31	98.81

Phenol = 0.1022 N
KI = 20% Solution by Weight
KOBr = 0.1016 N.
Thio = 0.1003 N.
HCl = 1.2 Sp. G.

The results obtained indicate that amounts of phenol as small as 0.000015 grams per cc. may be determined within one per cent by this method and with a reaction period of one minute.

Table VI shows that one minute shaking is sufficient by the method used for an accuracy not greater than four parts per thousand. Each test was run with a total volume of 100 cc. and in each the concentration of the various solutions were the same. The six determinations were a single series. All six are submitted, none rejected, thus giving a fair estimate of the amount of the error to be expected generally in a laboratory determination.

Table VI
Hypobromite.

No.	H_2O	HCl	C_6H_5OH	KOBr	Time Min	KI	Time Min	$Na_2S_2O_8$	Per cent
1	61	5	15	19	1	5	3	3.99	100,3
2	"	"	"	"	"	"	"	3.98	100.4
3	"	"	"	"	"	"	"	4.02	99.6
4	"	"	"	"	"	"	"	4.00	99.8
5	"	"	"	"	"	"	"	4.01	99.7
6	"	"	"	20	"	"	"	5.00	99.8

Phenol = 0.1022
KOBr = 0.1016
$Na_2S_2O_3$ = 0.1003
HCl = 1.2 Sp. G.
KI = 20% solution by weight.

Attention is called to the fact that in each of these tables, the phenol was first diluted with water before the hypobromite solution was added to it. This is of interest because of the fact that a number of authors state that in the determination of phenol by bromine,[1] a red compound is formed in the white precipitate which is probably tetrabromphenoquinone. Only once or twice in all our determinations did the pricipitate show even a light pink shade, never yellow which would indicate tribrom phenol bromide, and in all the other cases the precipitate was perfectly white. In every case where the red compound is mentioned the phenol solution was used with greater concentration than N/100, it was found that by diluting the phenol to approximately N/100 reduced the formation of this compound to zero and possibly increased the accuracy of the method.

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1) Beckurts, Archiv. Pharm. V. 24, 561, 1886 from J.S.C.I. V. 5, 546. 1886.

THE BROMIDE-BROMATE METHOD

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This method is similar in most respects to the hypobromite method. For this method instead of using a solution of hypobromite as in the first case, a solution consisting of a mixture of potassium bromide and potassium bromate (Koppeschaar's solution) was used. This is the standard solution used by the United States Pharmacoepoeia and is made as follows: 3.5 grams of potassium bromate and 55 grams of potassium bromide were dissolved in water and then diluted up to one litre.

This solution has considerable advantage over the hypobromite solution in that it contains no free bromine and therefore does not have the objectionable odor of the hypobromite solution. Moreover, for the same reason, it is much more stable than this solution[1)] and does not require to be standardized with each operation. The chief objection to the use of the bromide solution, however, has been that, it was too slow. Koppe-

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1) See Part 5 of Summary Page 42.

schaar recommends 15 minutes shaking and the U. S. P. 30 minutes before the KI solution is added.

As shown by the following tables it is not necessary to shake for one-half hour to obtain an accuracy of three parts per thousand. The order of adding the solutions in each table is from left to right.

Table VII

Bromide Bromate

No.	H_2O	HCl	C_6H_5OH	Bromide Bromate	Time Min.	KI	Time Min.	$Na_2S_2O_3$	Per cent
1a	61	5	15	19	1	5	3	2.80	99.72
1b	"	"	"	"	1	"	"	2.75	100.04
2a	"	"	"	"	5	"	"	2.80	99.72
2b	"	"	"	"	5	"	"	2.77	99.92
3a	"	"	"	"	10	"	"	2.80	99.72
3b	"	"	"	"	10	"	"	2.79	99.79
4a	"	"	"	"	15	"	"	2.78	99.85
4b	"	"	"	"	15	"	"	2.77	99.92
5a	"	"	"	"	20	"	"	2.73	100.11
5b	"	"	"	"	20	"	"	2.80	99.72
5c	"	"	"	"	20	"	"	2.75	100.04
5d	"	"	"	"	20	"	"	2.82	99.60
6a	"	"	"	"	30	"	"	2.70	100.30
6b	"	"	"	"	30	"	"	2.74	100.11
7a	"	"	"	"	60	"	"	2.70	100.30
7b	"	"	"	"	60	"	"	2.71	100.30

Strengths of solution.

Phenol = 0.1022 N
Bromide-Bromate= 0.09493 N
Thiosulfate = 0.09816 N
KI = 20%
HCl = 1.2 Sp. G.

In Table VII constant volumes of water, phenol acid and bromide bromate solution were used, but the time of shaking varies. It will be noticed that for no test was there a greater error than 0.6 per cent and that with one exception all the results are within 0.3 per cent. The results obtained for one minute shaking are as accurate as those for 15 mm., 30mm., or 1 hour.

In order to confirm the one minute determinations, a series of five tests were run exactly similar to those in Table VII. The five results are submitted, none rejected, thereby giving an idea of the magnitude of the errors to be expected in an ordinary laboratory determination by this method.

The results, given below in Table VIII show an average error of 0.3%, the greatest error being 0.4%.

Table VIII
Bromide-bromate

No.	H_2O	HCl	C_6H_5OH	Bromide Bromate	Time Min.	KI	Time Min.	$Na_2S_2O_3$	Per cent
1.	61	5	15	20	1	5	3	5.81	100.4
2.	"	"	"	18	1	"	"	3.88	100.4
3.	"	"	"	18	1	"	"	3.90	100.2
4.	"	"	"	18	1	"	"	3.92	100.3
5.	"	"	"	18	1	"	"	3.90	100.2

Strength of Solutions in Table VIII

Phenol	=	0.08815 N
Bromide-bromate	=	0.09493 N
Thiosulfate	=	0.09816 N
KI	=	20%
HCl	=	1.2 Sp. G.

Table IX like table V varies the concentration of phenol with respect to the total volume, but keeps the relative quantity of bromide-bromate with respect to the phenol constant. In this table the time of shaking was taken as one-half hour. This length of time was chosen according to the U. S. P., as Table IX was completed before Tables VII and VIII.

Table IX
Bromide-bromate

No.	H_2O	HCl	C_6H_5OH	Bromide Bromate	Time Min.	KI	Time Mim.	$Na_2S_2O_3$	Per cent
1a	61	5	15	19	30	5	3	2.70	100.36
1b	"	"	15	19	"	"	"	2.74	100.11
2a	72	"	10	13	"	"	"	2.12	100.39
2b	72	"	10	13	"	"	"	2.15	100.10
3a	83.5	"	5	6.5	"	"	"	1.02	101.15
3b	83.5	"	5	6.5	"	"	"	1.08	100.00
4a	90.4	"	2	2.6	"	"	"	0.39	102.02
4b	90.4	"	2	2.6	"	"	"	0.43	100.05
5a	92.7	"	1	1.3	"	"	"	0.19	102.50
5b	92.7	"	1	1.3	"	"	"	0.21	100.58

Strength of Solutions in Table IX.

Phenol	=	0.1022 N
Bromide-bromate	=	0.09493 N
Thiosulfate	=	0.09816 N
KI	=	20%
HCl	=	1.2 Sp. G.

The results for one and two cubic centimeters of phenol are seen to be less concordant than those for larger amounts. However, as one drop is an error of 5% in one cc., and as the phenol solution was measured out from a burette and not weighed, the agreement is fairly good. The table shows that 0.000015 grams of phenol per cc. may be determined by this method with an error of two per cent. The method is probably much more sensitive than this if more dilute solutions are used.

From these tables we have come to the following conclusions: First, for work requiring an accuracy not closer than 0.3 per cent, it is unnecessary to shake the acidified phenol solution with Koppeschaar's solution (bromide-bromate) or with Lloyd's hypobromite solution for a longer time than one minute if a continuous shaker is used, and if the conditions of dilution etc. are those given

in the preceeding tables, no red or yellow compounds are observed in the white tribromphenol precipitate.

In addition to the above experiments, tests were run by the two methods to determine the error, which might be introduced in the determinations due to chemicals, evaporation of bromine due to the use of ordinary one-half litre bottles, method of working etc.

Thus, thinking that an error might be introduced by running the hypobromite solution into the phenol without shaking, assuming that the spot where the hypobromite entered would be alkaline and thus introduce an error, tests were run, but no appreciable effect was noticed in this case.

A series of six determinations to find the effect of titrating back with the thiosulphate after periods of 1, 2 and 3 minutes (continuous shaking) from the time when the KI was added, gave results which showed a maximum error of 0.5 per cent within themselves. Accordingly an error ofj not more than 0.5 per cent is introduced if the solution is only shaken 1 minute after adding the potassium iodide.

Blank experiments were run under the same conditions as the original determinations which showed that the maximum error introduced by the solutions, manipulation, bottles, etc. was 0.3 per cent.

SUMMARY

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(1) The results show that by the above methods of manipulation, either with the hypobromite or with the bromide-bromate solution, phenol determinations may be made within an error of 0.3 per cent with only one minute of shaking after the solution containing the bromine is added, i.e., the reaction period may be reduced from 30 minutes to 1 minute without sacrificing accuracy.

(2) The phenol in each case was diluted until it was approximately N/100 before the determination was made. The resulting precipitate with the hypobromite or bromide-bromate solution was white and flocculent in each case and the precipitate showed no traces of the red tetra-brom-phenoquinone or the yellow tri-brom-phenol bromide.

(3) In order to secure correct results, the phenol solution must be acid after the bromine is added. If it is alkaline, an error is introduced which increases as the concentration of the phenol in the solution diminishes.

(4) The error introduced by shaking the solution for only one minute after the KI solution is added the tirating back with thiosulphate is 0.5%. Three minutes shaking eliminates this error and longer shaking has no effect.

(5) The bromide-bromate solution has the advantage over the hypobromite of being permanent. When the solution used was first made, its strength was 0.09493 N. After three months duplicate tests gave 0.09495 N. The hypobromite solution, weakened one-third per cent every twenty-four hours.for the first few days after the solution was made. The bromide-bromate solution has not the unpleasant odor of free bromine.

DIRECTIONS

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In order to carry out the determinations of phenol according to the above methods, the following directions are given:

(1) Prepare one-half per cent by weight starch solution and a 20% potassium iodide solution and N/10 of sodium thiosulphate, hypobromite, or bromide-bromate.

Into a 500 cc. bottle, fitted with a ground glass stopper, put 60 cc. water, 5 cc. hydrochloric acid (sp.g. 1.2) and then add 15 cc. of the unknown phenol solution which is to be determined and which has previously been diluted to about N/10. Add quickly, enough N/10 hypobromite or bromide-bromate solution to make the solution yellow and then add in addition 10% of the amount already added. Place the stopper in the bottle and shake continuously for one minute. Add to the solution in the bottle 5 cc. potassium iodide solution (20%) and again shake for three minutes. Wash down the stopper and sides of the bottle and titrate the solution with

the N/10 thiosulphate, using starch solution as an indicator with which to determine the end point. The starch must not be added until enough thiosulphate has been added to make this solution almost colorless. The quantity of thiosulphate used represents the quantity of free iodine, and therefore the quantity of excess bromine. The difference between this quantity and the known quantity of bromine added gives the amount of solution present Each cc. of N 10 bromine used up equals 0.00156 grams of phenol.